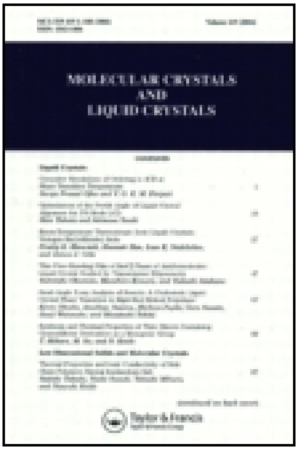

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MEASUREMENTS OF THE BEND AND SPLAY ELASTIC CONSTANTS OF A POLYMER LIQUID CRYSTAL BY THE FREDERIKS' DISTORTION

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The three elastic constants of a liquid crystal, K_{ii} (i=1,2,3) are fundamental measureable constants, which determine the way the material is held together and its response to an external stimulus. While extensive measurements have been carried out to determine the elastic constants of thermotropic liquid crystals,[1] very little is known about them in an important class of liquid crystals formed by macromolecules.

Lyotropic liquid crystals formed by polymers are biologically relevant and have been identified in a number of tissue and cell structures. They have also been found to be of technological importance in the manufacture of ultra high strength materials. Poly-γ-benzyl-L-glutamate (PBLG) forms an excellent model system for the study of lyotropic liquid crystals as many variables such as molecular weight, concentration and solvent nature can be easily controlled over wide ranges. Unlike the small molecule thermotropics, the elastic constants have been predicted to be highly variable.[2-4] The only detailed studies carried out so far have been measurements of the twist modulus, K_{22},[5-13] but no measurements on the other two moduli corresponding to splay (K_{11}) and bend (K_{33}) have been reported.

The most widely used method for the measurement of elastic constants in thermotropics has been the Fredericks' transition,[1] involving the deformation of an aligned, surface anchored sample of a liquid crystal by an electric or magnetic field. By varying the geometry employed, the various elastic constants can be determined from the critical field required to just begin the deformation of the sample. For the case of a magnetic field, the critical field $H_{ci} = (\pi/d)\sqrt{K_{ii}/\Delta\chi}$, i=1,2,3, where d is the thickness and $\Delta\chi$ the diamagnetic anisotropy. The application of this method to polymeric liquid crystals has been constrained by the fact that these systems are difficult to align on glass surfaces.

We have been able to obtain homeotropic alignment of polymeric liquid crystals between flat glass plates by the following procedure: the plates are soaked in chromic acid overnight, rinsed out in water followed by a short soaking in a weak solution of sodium bicarbonate to remove excess acid. This is followed by a thorough washing in running water and a rinse in deionized distilled water. The plates are then dried, first by blotting out with filter paper followed by about three hours in an oven at about 100°C. Sample cells are prepared by sandwiching PBLG solutions between the glass plates using mylar spacers to define the thickness. The cell is then screwed into a brass holder designed to be airtight to avoid solvent evaporation. About three to four hours are generally necessary for the sample to align itself homeotropically.

The solutions of PBLG are generally cholesteric liquid crystals. Uniform nematic textures are however obtained when the sample is confined in thin cells. Such a boundary induced transition has been observed in thermotropics[14] as well as in PBLG and poly-n-amyl glutamate liquid crystals.[15] The homeotropic alignment is generally lost for thicknesses larger than ∿10 μ.

Using a homeotropically aligned sample, we have measured K_{33} following the technique first used by Saupe.[16] The sample is placed between the poles of an electromagnet with the direction of orientation perpendicular to the field direction. A He-Ne laser is directed on to the sample along the uniaxial direction and an analyser and polarizer are placed on either side of the sample crossed at an angle of 45° with respect to the field direction. The transmitted intensity above the critical field is given by $I = I_o \sin^2(\delta/2)$, where

$$\delta = \frac{2\pi n_o d}{\lambda}\left\{1 - \frac{2H_c}{\pi H}\int_0^{\pi/2} dx \left[\frac{1+\kappa\sin^2\theta_m\sin^2 x}{(1-\sin^2\theta_m\sin^2 x)(1+\nu\sin^2\theta_m\sin^2 x)}\right]^{\frac{1}{2}}\right\} \tag{1}$$

λ is the wavelength, $\nu = (n_o^2-n_e^2)/n_e^2$, n_o and n_e are the ordinary and extraordinary refractive indices, $\kappa = (K_{11}-K_{33})/K_{33}$, and $H(>H_{c3})$ the magnetic field. The angle θ_m is the maximum deformation angle (obtained at the center of the sample and is given by the integral equation

$$\frac{Hd}{2}\left(\frac{\Delta\chi}{K_{33}}\right)^{\frac{1}{2}} = \int_0^{\pi/2} dx \left[\frac{1+\kappa\sin^2\theta_m\sin^2 x}{1-\sin^2\theta_m\sin^2 x}\right]^{\frac{1}{2}} \tag{2}$$

In the case of thermotropics, the birefringence $\Delta n = n_e - n_o$ is $\sim$0.2 and the consequent retardation δ, goes through a large number of multiples of π. The transmitted intensity therefore shows an oscillatory behavior above the critical field. In the case of this polymer liquid crystal, the birefringence is $\sim$0.004[17] and the phase retardation is less than π for usable values of the sample thickness. Figure 1 illustrates the effect on I(H) of a reduction of Δn keeping all other elastic and optical parameters fixed. It is seen that for birefringence values typical of this polymer liquid crystal, the intensity versus magnetic field plot is a broad featureless trace. The onset of the transition at H_{ci} is however evident.

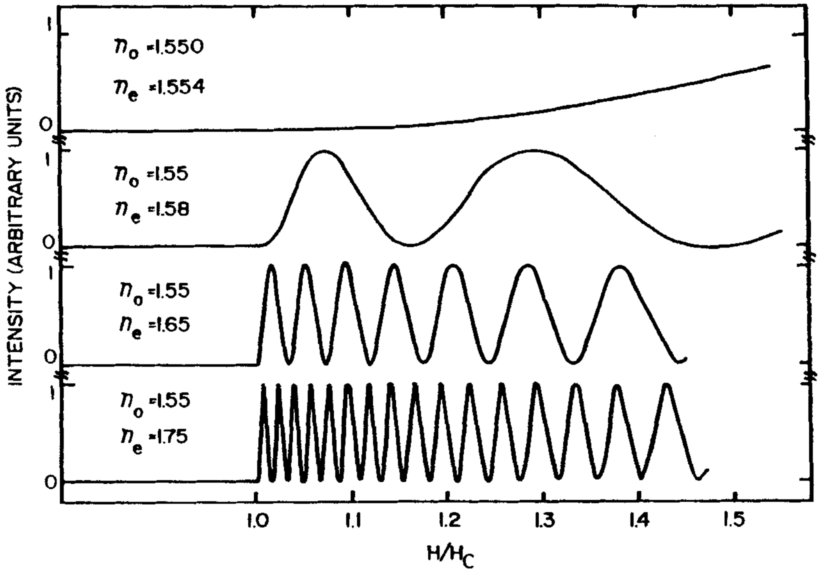

FIGURE 1 Intensity oscillations as a function of reduced magnetic field strength, H/H_c calculated on the basis of equations (1) and (2) with $K_{11}^c = 5.19 \times 10^{-7}$ dyne $K_{33} = 6.49 \times 10^{-7}$ dyne for various values of the birefringence, Δn. Note that as Δn decreases oscillations above H_c are reduced.

Our measurements for a liquid crystal formed by an 18% solution of PBLG (molecular weight = 296,000) in dioxane-6% TFA yields a K_{33} of $1.06 \pm 0.05 \times 10^{-9}$ dynes. Values of $\Delta\chi$ were obtained from the literature.[7,8] Trifluoroacetic acid (TFA) was added to reduce the viscosity and hence the response time to the magnetic field. An earlier work[8] found that there was no effect of such an addition on the twist modulus. We are currently investigating the effects on the other elastic moduli.

In thermotropic liquid crystals, K_{11} can be obtained from this geometry using the extrema values of the experimental I vs H curve. We have been able to obtain this additional modulus even in the absence of oscillating detail by fitting the entire I vs H curve to equations (1) and (2). The functions generated for different values of K_{11}, K_{33} being held constant at the above value, were normalized at the high field point till the best fit was obtained for all intermediate field strengths. This approach is justified by the fact that the shape of the I vs H curve changes with a change in K_{11}. This procedure yielded a value of $4.0 \pm 1.0 \times 10^{-8}$ dynes for K_{11}. Figure 2 shows the results of this fitting procedure.

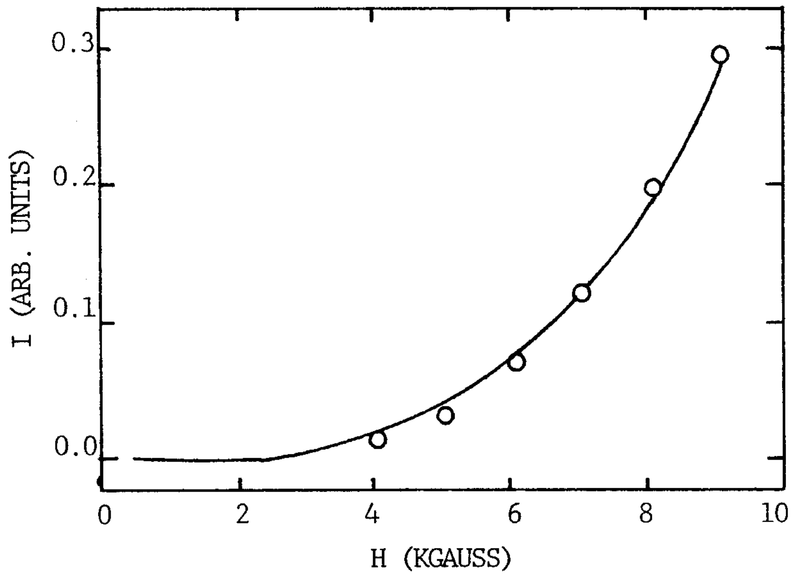

FIGURE 2 Transmitted intensity as a function of field strength for PBLG liquid crystal. The solid line is the experimental intensity and the circles are the calculated intensities for the best fit leading to the K_{11} value reported in the text.

Using this method we are exploring the effect of molecular weight and polymer-solvent interaction on the bend and splay elastic moduli.

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